

## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification<sup>4</sup> :

B05D 3/04

A1

(11) International Publication Number:

WO 90/00940

(43) International Publication Date:

8 February 1990 (08.02.90)

(21) International Application Number: PCT/US89/01731

(22) International Filing Date: 21 April 1989 (21.04.89)

(30) Priority data:

223,187

22 July 1988 (22.07.88)

US

(71) Applicant: DENNISON MANUFACTURING COMPANY [US/US]; 300 Howard Street, Framingham, MA 01701 (US).

(72) Inventors: ABBER, Herman ; 60 Brian Drive, Brockton, MA 02403 (US). EDWARDS, Robert, M. ; 4 Briar Drive, Milford, MA 01757 (US). SODAGAR, Eleanor, H. ; 75 Summerhill Avenue, Worcester, MA 01606 (US). ANEMAET, John, M. ; 58 Union Street, Millis, MA 02054 (US). GALANTE, Richard, J. ; 193 Highland Street, Milford, MA 01757 (US).

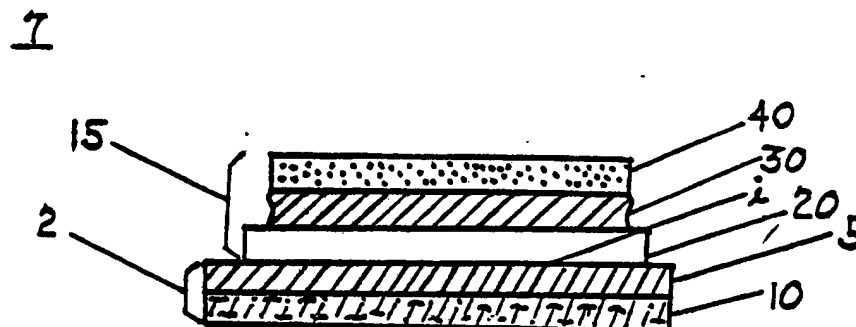
(74) Agent: JOSEPHS, Barry, D.; Dennison Manufacturing Company, 300 Howard Street, Framingham, MA 01701 (US).

(81) Designated States: AT (European patent), AU, BE (European patent), BR, CH (European patent), DE (European patent), DK, FI, FR (European patent), GB (European patent), IT (European patent), JP, KR, LU (European patent), NL (European patent), NO, SE (European patent).

Published

*With international search report.*

(54) Title: HEAT TRANSFERABLE LAMINATE



## (57) Abstract

An improved release system for heat transferable laminates wherein a transferable substrate (15) which contains a design layer (30) is transferred from a carrier web (2) onto an article such as a plastic bottle or container upon application of heat and pressure. The carrier web (2) includes a nonwax layer (5). The improved release system (5) includes a noncellulosic alkyd thermoset layer portion of the carrier web in contact with and adhered to a nonwax transfer layer portion of the transferable substrate (15). The improved release layer (5) is preferably a melamine modified noncellulosic alkyd which on curing exhibits thermoset properties. The transferable substrate transfers to the article upon application of heat to the carrier while the article contacts the laminate. The transferred substrate on the article is clear and exhibits improved scuff and abrasion resistance. The nonwax layer does not contain wax and may exhibit thermoplastic or thermoset properties.

***FOR THE PURPOSES OF INFORMATION ONLY***

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	ES	Spain	MG	Madagascar
AU	Australia	FI	Finland	ML	Mali
BB	Barbados	FR	France	MR	Mauritania
BE	Belgium	GA	Gabon	MW	Malawi
BF	Burkina Faso	GB	United Kingdom	NL	Netherlands
BG	Bulgaria	HU	Hungary	NO	Norway
BJ	Benin	IT	Italy	RO	Romania
BR	Brazil	JP	Japan	SD	Sudan
CA	Canada	KP	Democratic People's Republic of Korea	SE	Sweden
CF	Central African Republic	KR	Republic of Korea	SN	Senegal
CG	Congo	LI	Liechtenstein	SU	Soviet Union
CH	Switzerland	LK	Sri Lanka	TD	Chad
CM	Cameroon	LU	Luxembourg	TG	Togo
DE	Germany, Federal Republic of	MC	Monaco	US	United States of America
DK	Denmark				

HEAT TRANSFERABLE LAMINATE  
BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a heat transferable label and improved release composition therefor.

2. Description of the Prior Art

Prior art heat transferable labels for imprinting designs onto an article typically involve decorative laminates consisting of a paper base sheet or carrier web coated with a wax or polymeric release layer over which a design is imprinted in ink.

U.S. Patent No. 3,616,015 (Kingston) is illustrative of the prior art. In U.S. Patent No. 3,616,015 a label-carrying web, such as a paper sheet, includes a heat transferable label having a wax release layer affixed to a surface of the paper sheet and an ink design layer superimposed onto the wax release layer. In the heat transfer labeling process for imprinting designs onto articles, the label carrying web is subjected to heat and the laminate is pressed onto an article with the ink design layer making direct contact with the article. As the web or paper sheet is subjected to heat, the wax layer begins to melt and allows the design layer to transfer to the article. A portion of the wax release transfers to the article along with the design image. After transfer of the design to the article, the paper sheet is immediately removed leaving the design firmly affixed to the surface of the article with the wax layer exposed to the environment thereon. The wax layer thus serves two purposes in that it provides release of the transferable label from the web upon application of heat to the web and also forms a clear protective layer over the transferred ink design. After transfer of the label to an article, the transferred wax release layer is typically subjected to post-flaming which produces an optically clear

-2-

protective layer over the ink design and enhances the protective properties of the transferred wax release.

The additional step involving post-flaming is accomplished by subjecting the transferred wax layer to jets of high temperature gas either as direct gas flame or as hot air jets to produce wax surface temperatures of about 300<sup>0</sup>F to 400<sup>0</sup>F for a period of time sufficient to remelt the wax coating without substantially heating the article to which the label has been transferred. Upon cooling of the remelted wax coating through use of ambient or forced-cooled air, the cooled wax layer solidifies to form a clear, smooth protective coating over the ink design.

Although the heat transferable label disclosed in this reference may be utilized for decorating a wide variety of different articles, typically plastic bottles, there is a degree of hazing or "halo" noticable over the transferred label when the transfer is made onto clear plastic materials, despite use of post-flaming. The "halo" effect is caused by transfer of a portion of the wax release layer from the paper carrying sheet onto the article along with the ink design layer. Although the transferred wax layer has the beneficial effect of providing a protective coating over the transferred ink design, the nature of the wax coating is such that it provides some halo around the outer borders of the transferred ink design layer. Although wax based release layers have produced optically clear protective layers over the ink design and provide a high degree of protection for the transferred ink design, they are nonetheless subject to scuffing and abrasion because of the inherent nature of the wax material.

U.S. Patent No. 3,922,435 (Asnes) discloses a heat transferable label which is directed to replacing the wax based release layer with a nonwax resin thus avoiding the "halo" effect long associated with the use of wax based compositions. Asnes refers to this type of release layer as a dry release since it does not transfer to the article

along with the ink design layer when heat is applied to the heat transferable laminate as the laminate is in contact with the article. Asnes discloses an embodiment wherein the release layer is coated onto a backing sheet, and a printed lacquer layer is coated over the release layer and then a design print layer is coated over the lacquer layer. A heat activatable adhesive overprint layer is coated over the design layer. Asnes discloses that either or both the dry release layer and/or the lacquer layer may contain a thermoset polymeric resin which will not become molten upon application of heat as used in the typical heat transfer temperature range, for example 300F to 450<sup>0</sup>F. (Col. 9, lines 3-8). The reference Asnes discloses a list of thermoset resins which are crosslinked resins for the release layer for which resins are preferably selected from the group consisting of acrylic resins, polyamide resins, polyester resins, vinyl resins, epoxy resins, epoxy-acrylate resins, allyl resins and aldehyde resins. (Col. 5, lines 34-38). Asnes also mentions that the thermoset resin for the release layer may also include copolymers of aminoaldehydes with alkyds, or styrenated alkyds (Col. 5, lines 44-46). Asnes also indicates that copolymers of hexamethoxymethyl melamine and cellulosic esters, preferably cellulose acetate butyrate or cellulose acetate may give optimum results. (Col. 5, lines 51-54). Asnes also teaches that where the thermoset or other resin is in the release coat, a preferred material for the lacquer layer printed thereon is a cellulosic ester, such as cellulose acetate. (Col. 5, lines 55-58).

Although various chemical classes of resins having thermoset properties are referenced in Asnes in the description therein, it has nonetheless proved to be a very difficult problem to find a combination of nonwax thermoset release and lacquer layer to be coated thereon, which satisfies the very large number of properties simultaneously that are required and demanded of heat

-4-

transferable laminates in the modern day market. The bond between the thermoset release coating and the lacquer coating must diminish significantly when heat is applied to the laminate so that the transferable portion of the laminate separates cleanly from the release layer without taking with it any portion of the release. In actual practice it has proved difficult to find a combination of thermoset resins for the release and lacquer coating layer which prevents any discernible "pickoff" of the release layer during transfer of the ink design layer to an article during the heat transfer process. It has also proved difficult with thermoset release systems to achieve the degree of clear glossy images of the transferred ink design layer which are comparable to that attained with conventional wax-based release systems. It has also proved to be particularly difficult to achieve a "smooth interface" between the thermoset release layer and the lacquer coating layer at the very moment of transfer of the design layer and lacquer layer to the article. At the very moment of transfer any imperfection in the degree of smoothness and surface continuity at the interface between the release layer and the lacquer coating layer result in a lessening in the gloss quality of the transferred design image. Additionally, the lacquer coating must at all times resist penetration by the ink design. It also must exhibit a high degree of clarity and a high degree of scuff and abrasion resistance after it has been transferred along with the design image to the receiving article. It has been a very difficult problem to formulate a nonwax release system which exhibits all of these required properties simultaneously.

Accordingly, it is an object of the present invention to provide an improved nonwax base release system for heat transferable laminates which permits transfer of an ink design image from a carrier web to an article, in particular to a plastic article. It is an important object to provide a release system which provides a

protective coating over the transfer ink design image such that the transferred image shows improved resistance to abrasion and scuffing while maintaining a high degree of optical clarity.

It is a further object to provide an improved release system and heat transferable laminate for use in transfer of a design image from a carrier web to a plastic article wherein the problem of wax "halo" around the transferred image has been eliminated. A related object is to provide an improved release system for heat transferable laminates which provides a protective coating for the transferred image which is also resistant to common solvents.

#### SUMMARY OF THE INVENTION

In accomplishing the foregoing and related objects the invention provides a heat transferable laminate having an improved release system. The heat transferable laminate of the invention includes a carrier sheet, typically of paper, and a transferable substrate affixed to the carrier sheet. The carrier sheet includes a nonwax thermoset release layer coated over the paper sheet. The nonwax release layer is advantageously formed by the crosslinking of an alkyd resin with melamine to produce a thermoset release. The nonwax release layer is a noncellulosic alkyd resin formed of the crosslinking reaction of an alkyd polymer with methoxy melamine to yield the thermoset release layer. The alkyd polymer employed is preferably of the type formed by the thermosetting reaction product of a hydroxy-functional polyester with a drying oil. The preferred hydroxy-functional polyester is the copolymer of monoethylenically unsaturated monomers such as a solution copolymer composed of 2-hydroxyethyl acrylate, lauryl methacrylate and styrene. In place of the styrene component methyl methacrylate may be used or else mixtures of styrene and methyl methacrylate. The preferred polyester thus is of the type and composition disclosed in U.S. patent 4,654,270, col. 3, lines 15-28. The drying oil

-6-

used is typically safflower but may also be tung, linseed, castor, safflower, tall oil fatty acid, soya cottonseed, peanut, castor and coconut oil.

When melamine preferably hexamethoxymethyl melamine is added to the alkyd polymer together with suitable crosslinking catalyst, the mixture is coated onto the paper carrier sheet. The coating is then subjected to curing, for example by convective hot air. During curing the melamine becomes crosslinked with the alkyd polymer to form a highly desirable thermoset release layer on the paper carrier. Applicant has determined that distinctively superior properties are achieved when the release layer is formed in this manner.

The transferable substrate portion of the transferable laminate is formed of a nonwax lacquer transfer layer, an ink design layer over the lacquer coating transfer layer and a heat activatable adhesive layer over the ink design layer. The transferable substrate is formed by coating each one of these layers in turn beginning with the lacquer coating transfer layer over the thermoset release layer of the carrier web to form a composite laminate.

The thermoset release of the type above described has proved to exhibit exceptional release properties with a number of different types of lacquer transfer layers which maybe either thermoset or thermoplastic in nature. However, applicant has determined that the aforementioned thermoset release exhibits particularly favorable release characteristics with transfer lacquers which have as the principal component therein vinyl resins such as polyvinylidene chloride, acrylics such as ethylmethacrylate, or copolymers of vinyl chloride and vinyl acetate, or a polyester, in particular a polyester which is a saturated linear aromatic polyester, preferably a modified polyethylene terephthalate.

As heat and pressure are applied by a heat source to the composite laminate in contact with an article, such as a plastic container, the transferable substrate releases



cleanly from the thermoset release layer of the carrier and transfers to the article, typically a plastic bottle or container being decorated. The heat source applied is typically a heated metal platen or heated platen roller having a surface temperature between about 275°F to 425°F. The release system of the invention has the property that on application of the heat source to the exposed side of the carrier sheet while the transferable substrate is in contact with an article, the transferable substrate releases cleanly from the carrier to the article without taking with it any discernible portion of the thermoset release layer. Also the release system has the additional property that on transfer of the transferable substrate, no discernible portion of the lacquer coating layer remains in contact with the thermoset release layer. So clean a separation between the thermoset release and the lacquer transfer layer that no discernible portion of either layer remains on the other is believed to be a distinct improvement of prior art systems that have attempted to employ a thermoset resin for the release. The resulting transferred substrate on the article shows a clear transfer design image adhered permanently to the article. The transfer design image is protected by the lacquer coating transfer layer which also transferred to the article. The transferred lacquer coating layer covers the design image and provides a clear protective coating which affords markedly improved abrasion and scuff resistance for the transfer design image. The degree of abrasion resistance afforded by the transferred lacquer coating is greater than what has heretofor been achieved by use of a wax base release in contact with a carrier. The tough protective coating also exhibits excellent resistance to attack by household alcohol and common solvents often found in cosmetics and toiletries.

The present release system of the invention has the additional advantage over wax base release systems in that

-8-

it eliminates the wax "halo" effect around the borders of the transferred design image. The wax "halo" effect eliminated by the present release system has been long associated with wax base release formulations.

Another aspect of the invention is that it has been determined that the inclusion of a lubricating agent, in particular lecithin, into the coating formulation before it is coated onto the release layer, enhances the smoothness of the surface of the lacquer coating after it has transferred onto a receiving article. Thus, when a lubricating agent is employed, applicant has discovered that a smoother and consequently markedly glossier transfer coating results on transfer to the receiving article. In effect, since the transfer lacquer coating forms a protective layer over the transferred design image, the design image appears noticably glossier when the lubricating agent is employed in the lacquer coating layer.

#### BRIEF DESCRIPTION OF THE DRAWING

Fig. 1 is an illustration of a preferred embodiment of the composite heat transferable laminate.

#### DETAILED DESCRIPTION

A preferred embodiment of the heat transferable laminate 7 of the invention, as illustrated in Fig. 1 is composed of a carrier web 2 and a transferable substrate 15. The carrier web is composed of a support sheet 10, typically of paper overcoated with a nonwax release layer 5. The nonwax release layer 5 is advantageously composed of an alkyd resin which is cured to produce a thermoset resin. The transferable substrate 15 as shown in Fig. 1 is composed of a lacquer transfer coating 20 which is overcoated with an ink design layer 30 which is in turn overcoated with a heat activatable adhesive layer 40.

As heat from a hot platen or a hot platen roller is applied to the exposed side of support sheet 10 while the

adhesive layer 40 of laminate 7 comes into contact with a bottle or article to be decorated, transferable substrate 15 separates cleanly from carrier web 2 and transfers onto the article.

The transferable laminate 7 of the invention has the property that the transferable substrate 15, during transfer to the article, separates cleanly from the thermoset release layer 5 at the interface i without taking with it any portion of release layer 5. This result is achieved with application of a heated platen (not shown) to the exposed side of support sheet 10 wherein the heated platen has an average surface temperature of between about 275°F to 425°F, preferably between about 300°F to about 425°F. The term "wax" as used herein shall have its normal dictionary definition as in G. Hawley. The Condensed Chemical Dictionary, 10th Edition, Van Nostrand Reinhold Company. The thermoset release layer 5 is a nonwax layer in that it does not contain waxes.

The thermoset release layer 5 is composed of an alkyd resin. The alkyd resin release layer 5 is formed by coating a liquid mixture containing an alkyd polymer, melamine and cross linking catalyst onto support sheet 10 using conventional gravure coating methods. This coating is subsequently subjected to convective heat in order to cure and cross-link the alkyd polymer with the melamine to produce a solid thermoset coating layer over the support sheet 10. The melamine used in the release layer 5 coating mixture is a methoxy melamine, preferably hexamethoxymethyl melamine and the preferred cross linking catalyst is paratoluene sulfonic acid.

The alkyd polymer is formed in conventional manner by reacting a polyester and oil. The polymerization reaction may be carried out by cooking the polyester and oil for a period of time in a suitable vat preferably employing a catalyst such as sodium hydroxide under constant agitation in order to achieve polymerization of the polyester and

-10-

the oil. The alkyd polymer thus formed is then cooled and as aforesated melamine preferably hexamethoxymethyl melamine is added. The melamine is left in the mixture in unreacted form. This mixture is thus referred to as a methoxymelamine modified alkyd liquid mixture. Prior to coating the melamine modified alkyd mixture onto support sheet 10 a catalyst preferably a paratoluene sulfonic acid catalyst is added and mixed into the modified alkyd resin until a homogeneous liquid mixture is achieved. The paratoluene sulfonic acid may be obtained under the trademark Cycat 600 from American Cyanamid Company.

The polyester employed in the present alkyd polymer is a hydroxy-functional resin preferably of the type disclosed in U.S. patent 4,654,270 herein incorporated by reference. The polyester is preferably a hydroxy-functional resin of the type and preferred composition disclosed in U.S. Patent 4,654,270 at col. 3, lines 15-28. It should, therefore be noted that the polyester used herein is not a cellulosic ester and not cellulose acetate butyrate or cellulose acetate as disclosed in prior art patent U.S. 3,922,435, at col. 5, lines 51-54. The preferred polyester is instead a hydroxy-functional polyester as disclosed in U.S. Patent 4,654,270 (col. 3, lines 20-28) which is the copolymer of monoethylenically unsaturated monomers, such as a solution copolymer of 15% 2-hydroxyethyl acrylate, 40% lauryl methacrylate and 45% styrene. The styrene content in this mixture may be replaced with methyl methacrylate or any mixture of styrene and methyl methacrylate as disclosed in this reference. The preferred melamine is hexamethoxymethyl melamine disclosed in U.S. Patent 4,654,270 at col. 1, line 34. The drying oil used in the thermoset reaction is typically safflower oil but may also be selected from tung, linseed, dehydrated castor, safflower, tall-oil fatty acid, soya cottonseed, peanut, castor, olive and coconut. These are known oils used in the manufacture of alkyd resins and are referenced in this context in the

Encyclopedia of Polymer Science and Technology, John Wiley & Sons, Inc. 1964, Vol. 1, p. 684.

The alkyd polymer mixture formed by reaction of the above referenced preferred ester may be readily obtained from DeSoto, Inc. DePlaines, Illinois. The alkyd polymer mixture can be obtained from DeSoto, Inc. with the melamine preferably hexamethoxymethyl melamine added in unreacted form to the mixture as above described. This mixture is referred to by DeSoto as a methoxy melamine modified alkyd mixture.

After paratoluene sulfonic acid catalyst is added to the methoxy melamine modified alkyd mixture, the mixture is coated onto support sheet 10 and the coating is exposed to convective heat by passing the coating through a convective oven operating at about 350°-450°F for sufficient time to achieve curing and crosslinking of the resin with the melamine. It is noted that the melamine additive is the crosslinking agent for the alkyd. The alkyd is said to be modified by the addition of melamine. The melamine does not react until after the release is coated onto the paper substrate and cured in a convective oven. In this manner the coating becomes crosslinked to produce the thermoset release layer 5.

In Applicant's preferred system the lacquer coating transfer layer 20 has the property that during heat transfer at desirable platen temperatures between 275°F to 425°F, transferable substrate 15 separates cleanly from the thermoset release layer 5 without leaving behind on release layer 5 any discernible portion of the lacquer coating transfer layer 20.

The heat transfer laminate of the invention satisfies a number of additional requirements simultaneously. The nonwax thermoset release layer 5 is easily coated onto the support sheet 10 by conventional gravure printing methods. Coating of the lacquer transfer layer 20, ink design layer 30 and the heat activatable transfer layer 40 is readily accomplished in sequence by employing gravure

-12-

methods, but other printing methods such letter press, flexographic, or screen printing methods are also suitable.

Clean separation of the transfer coating 20 from the thermoset release layer 5 is achieved without leaving any discernible portion of either layer on the other when the heated platen or heated platen roller temperature is in the range between about 275°F to 425°F typically 300°F to 425°F and preferably 275°F to 350°F. The clean separation of the transfer coating 20 from the thermoset release layer 5 during the heat transfer process without leaving any discernible portion of either layer on the other is considered by applicant to be a significant achievement.

A preferred embodiment of the release system of the invention, which is the combination of the thermoset release layer 5 in contact with lacquer transfer coating 20, has the important additional property that it fully eliminates the problem of wax "halo" around the border of the transferred design image. The problem of wax "halo" has been long associated with wax based release formulations.

The problem of the wax "halo" effect is eliminated by the release system of the present invention since no discernible portion of the thermoset release layer 5 remains adhered to the transferable substrate 15 as the substrate 15 transfers onto the receiving article. This avoids a longstanding problem associated with wax base release layers which have a tendency to form a wax "halo" effect around the border of the transferred ink design image since a portion of the wax release in such systems transfers to the article along with the ink design.

Upon transfer the lacquer coating layer 20 forms a tough, clear protective coating over the ink design layer 30 on the receiving article. The transferred protective coating 20 shows marked improvement in abrasion and scuff resistance than that which has been achieved by wax based

release layers, for example, of the type described in U.S. Patent No. 3,616,015.

Upon transfer, the protective coating, namely coating layer 20 over the transferred ink design layer 30 exhibits marked improvement in abrasion resistance over wax based systems such that if one were to attempt to finger nail scratch the surface using moderate pressure no discernible scratch marks or abrasions would be left behind on the protective layer 20 covering ink design layer 30 on the article. This degree of abrasion resistance is quite difficult to achieve using a wax based release formulation even though improvements to wax base formulations have been made. A wide range of plastic articles can be used as the receiving surface. However, especially good results are obtained with rigid relatively smooth plastic containers of any shape or curvature, typically flat, cylindrical, oval, tapered and various other shapes. These plastic articles may be typically of high density polyethylene, polypropylene, polystyrene and polyvinylchloride. However, most other common plastics may be employed for the receiving article irrespective of whether they are thermoplastic or thermosetting.

Another advantage of the present invention is that it does not require heat transfer operating temperatures which depart from conventional platen temperatures between about 300°F and 425°F for transfer of the design imprinted heat transferable laminate onto plastic articles. Additionally, in the present invention, the platen temperature may be as low as about 275°F. These desirable platen temperatures in a range between about 275°F to 425°F have also been alluded to in commonly assigned patent application Serial No. 181,090 filed April 13, 1988 which patent application discloses a particular class of thermoplastic release layer and not the thermoset release layer 5 as described in the present patent application. The release system of the present invention may be employed with conventional decorator apparatus as well,

-14-

for example, as alluded to in U.S. Patent 3,616,015. When a wax based release system is used, post-flaming is required. The nonwax based release system of the present invention additionally eliminates the requirement for post-flaming the lacquer transfer layer 20, after it has transferred onto the article as part of transfer substrate 15.

Although post-flaming can be employed to improve the durability of the transfer substrate 15 on the article, it is not required. The elimination of the requirement of the post-flaming step is an additional improvement over processing required when conventional wax base release layer, layers are employed for example, as described in U.S. Patent 3,616,015. Such wax base release layers typically require exposure to jets of hot gas either as direct gas flame or as hot air jets for a period of time sufficient to remelt the wax in order to improve the clarity, smoothness and glossiness of the wax base protective coating, formerly the release layer, after the transferable substrate has been transferred onto a receiving article. The elimination of the need for post-flaming is a direct result of the improved release system of the invention which does not employ any waxes in either the thermoset release layer 5 or lacquer coating transfer layer 20.

The lacquer transfer layer 20 which has produced all of the aforementioned desirable properties in conjunction with use of the thermoset release layer 5 may itself be either thermoset or thermoplastic. A specific preferred formulation for a thermoset lacquer transfer layer 20 is given in Table I as formulation A and B. A specific thermoplastic formulation for the transfer layer 20 is given as formulation C in Table I. The formulation C is essentially identical to the formulation earlier disclosed in commonly assigned U.S. Patent application Serial No. 181,090, filed April 13, 1988.



-15-

TABLE IRELEASE LAYER (5):WT%

(e.g.,			
Methoxy melamine modified alkyd)			100
cured after coating on support sheet 10.			

FORMULATION ALACQUER COATING TRANSFER LAYER (20)

Primary Resin			
(e.g., SARAN F310			48.2
polyvinylidene chloride			

Secondary Resin			
(e.g., ELVACITE-2042			48.2
ethylmethacrylate)			

Crosslinking Agents			
(e.g., CYMEL 303			2.4
hexa methoxymethylamine)			
(e.g., CYCAT 4040			
paratoluene sulfonic acid			

Lubricating Agent			
(e.g., ALCOLEC S lecithin)			<u>1.0</u>
	TOTAL		100.0

SOLVENTS

Methyl Ethyl Ketone			59.6
---------------------	--	--	------

Toluene			39.7
---------	--	--	------

Isopropanol (Diluent			
for Crosslinking Agent)			<u>0.7</u>
	TOTAL		100.0

TABLE I (Cont'd)FORMULATION BLACQUER COATING TRANSFER LAYER (20):

	WT%
Primary Resin (e.g., UCAR solution vinyl resin type VAGH polyvinylchloride polyvinylacetate copolymer with hydroxy functionality)	40.3
Secondary Resin (e.g., ELVACITE-2042 ethylmethacrylate)	40.3
Crosslinking Agent (e.g., CYMEL 303 hexamethylmethoxymelamine)	2.0
(e.g., CYCAT 4040 paratoluene sulfonic acid)	0.2
Lubricating Agent (e.g., ALCOLEC S lecithin)	1.0
Plasticizer (e.g., KETJENFLEX-MS80 arylsulfonimide)	<u>16.2</u>
TOTAL	100.0

SOLVENTS

	<u>WT%</u>
Ethylacetate	74.7
Toluene	24.9
Isopropanol (Diluents for Crosslinking Agent)	<u>0.4</u>
TOTAL	100.0

TABLE I (Cont'd)

FORMULATION C:

LACQUER COATING TRANSFER LAYER (20):

	<u>WT%</u>
Primary Resin (Matrix) (e.g., Polyester VITEL PE-200)	85
Castor Oil (AA USP refined grade)	7
Polymetric Plasticizer (e.g., ESTANE 5715 Thermoplastic polyurethane)	<u>8</u>
TOTAL	100

SOLVENTS

	<u>WT%</u>
Toluene	21
Methylethylketone	65
Ethylacetate	<u>14</u>
TOTAL	100

-18-

The patent application, Serial No. 181,090 is commonly assigned to the same assignee as the present patent application. The formulation C, or lacquer coating transfer layer 20 was disclosed in commonly assigned patent application Serial No. 181,090 for use in conjunction with a polyolefin release layer and not in conjunction with use with the alkyd based release layer 5 as described in the present patent application.

The formulation A, shown in Table I, shows a coating mixture of resins in a solvent system which are coated onto release layer 5 using the conventional gravure printing method. The coating is then passed through a convective oven operating at about 250<sup>0</sup>F for sufficient time to evaporate the solvent and bring about curing and cross- linking of the coating to form a thermoset lacquer transfer layer 20. The preferred formulation A, shown in Table I for lacquer transfer layer 20, is composed of a primary resin, preferably a polyvinylidene chloride resin commercially available under the trademark SARAN F310 from the Dow Chemical Company and a secondary resin preferably ethylmethacrylate available under the trademark ELVACITE-2042 from the DuPont Corp. Crosslinking agents, preferably hexamethylmethoxymelamine and paratoluene-sulfonic acid are added to the formulation to cause at least the primary resin to crosslink and cure when the coating is passed through convective ovens. The crosslinking agent hexamethylmethoxymelamine is commercially available under the trademark CYMEL 303 from the American Cyanamide Company and the crosslinking agent paratoluenesulfonic acid is available under the trademark CYCAT 4040 from The American Cyanamide Company.

Applicant has determined that the addition of a lubricating agent, preferably lecithin promotes a smoother surface of the transfer layer 20 as it transfers from release layer 5 onto a receiving article. The solvent shown in Formulation A are conventional solvents for the

resin and crosslinking agents. These solvents permit attainment of a homogeneous mixture for Formulation A so that it may be readily coated onto release layer 5 using conventional gravure coating techniques. Lacquer transfer layer 20 may be employed as well without the lubricating agent.

Applicant has attained a marked improvement in the degree of surface smoothness of layer 20 when the lubricating agent, preferably lecithin, is employed in the formulation. The enhanced surface smoothness of transfer layer 20 imparts a discernible higher gloss to the transferred ink design layer when transferable substrate 15 is transferred to the receiving article. The increased gloss of the transferred lacquer layer 20 gives the ink design 30 a more appealing appearance than if the lubricating agent were not used in the formulation. It is theorized that the increase in surface smoothness of the transfer layer 20 is the result of an increase in smoothness of the interfacial surface *i* between thermoset release layer 5 and lacquer transfer layer 20 when heat is applied to support sheet 10.

It is theorized that as heat is applied to support sheet 10, the lubricating agent becomes activated and migrates to the interfacial surface *i* at the moment that transferable substrate 15 transfers from release layer 5 onto a receiving article. Since the transfer layer 20 transfers along with ink design layer 30 to the receiving article, the increase in surface smoothness of transfer layer 20 is believed to account for the overall increase in gloss of the transferred ink design 30.

Another preferred thermoset formulation for transfer layer 20 is shown as Formulation B in Table I. This preferred formulation is similar to that of Formulation A except that a different primary resin is employed and a plasticizer is also added to the formulation. The primary resin shown in Formulation B is a polyvinylchloride and, polyvinylacetate copolymer with hydroxy functionality to

-20-

permit cross linking on curing. This resin is commercially available under the trademark UCAR solution vinyl resin type VAGH available from Union Carbide Corp. The preferred plasticizer is an arylsulfonimide such as that available under the trademark KETJENFLEX-MS80 from the Akzo Chemie, a Netherlands Company.

The mixtures shown in formulation A and formulation B are each prepared by simply mixing listed components at ambient condition using conventional electric mixers for about an hour typically or until a homogeneous is achieved. Typically the solvents are added to an empty mixing vat first and then the components blended and mixed for a short time by blending in the components in the same order in which they appear in the Table. The cross linking agents are preferably added last and diluted first with isopropanol before addition to the mixture. In producing the coating mixture, the solvents shown in Formulation A and Formulation B are added in a ratio of about 3 parts total solvent to about 1 part solids wherein the solids are defined as all the components other than the listed solvents.

Thus, prior to coating the homogeneous mixture onto release layer 5, the mixture may again be diluted somewhat, typically to obtain a mixture of about 4 to 5 parts solvent to 1 part solids so that the mixture can be easily coated onto release layer 5 using conventional gravure coating techniques. After the Formulation A or Formulation B for transfer layer 20 is coated onto thermoset release layer 5 the coating is subjected to convective heat by passing it through conventional convective ovens operating typically at about 250°F to evaporate the solvents and simultaneously cause curing and cross linking of the resin in the formulation. It is believed that the primary resin is the resin that becomes crosslinked in the curing operation. The secondary resin is believed to contribute to the overall properties of hardness and durability to transfer layer 20. The cured

transfer layer 20 is not believed to be involved in the crosslinking reaction, at least not to the same degree as the primary resin. Although the cured transfer layer 20 employing formulation A and B is crosslinked and largely thermoset in character it does exhibit some thermoplastic characteristics as well in that it does soften somewhat and becomes somewhat pliable when heated.

On transfer of layer 20 along with ink design layer 30 formulation A and formulation B each impart all the aforementioned desirable characteristics to the transferred ink design layer. Specifically, the formulation A and B each provide a high gloss transfer layer 20 of high surface smoothness, high optical clarity, and markedly improved scuff and abrasion resistance when compared to wax based systems. These properties are all attained without transfer of any discernible portion of release layer 5 along with transfer layer 20. This is in distinct contrast to wax based release systems which split and transfer along with the design image to a receiving article.

Another preferred formulation is shown as Formulation C for the lacquer coating transfer layer 20. Formulation C is completely thermoplastic in character. Formulation C is composed of a primary resin, an oil and preferably a polymeric plasticizer additive. The primary resin is preferably a polyester resin, that is a saturated linear aromatic polyester, preferably modified polyethylene terephthalate such as that available under the trademark VITEL PE-200. This particular polyester resin is manufactured and available from the Goodyear Chemical Company of Akron, Ohio. The oil additive is a nondrying oil, preferably castor oil, preferably AA USP refined grade which is available in the commercial market from CAS CHEM COMPANY, Dayonne, NJ. The VITEL resin and castor oil are admixed in a suitable solvent system as shown in the Formulation C. The castor oil is present in relatively small quantities. The castor oil percent by weight of the

-22-

dry transfer coating 20 (on a solvent-free basis) should be between about 1.0 percent and about 15 percent by weight. The addition of castor oil to the thermoplastic formulation C has been determined to promote the release effect between the thermoset release layer 5 and the predominately polyester lacquer coating layer 20. Inclusion of the nondrying oil such as castor oil also is believed to enhance the degree of smoothness and thus gloss of the transferred layer 20.

It is theorized that as a heat from a hot platen is applied to support sheet 10 while adhesive layer 40 of laminate 7 contacts a receiving article, the nondrying oil becomes activated and migrates to the interfacial surface i between thermoset release layer 5 and lacquer transfer layer 20. This phenonomon is believed to promote clean transfer of lacquer transfer layer 20 from thermoset release layer 5. The addition of polymeric plasticizer such as a thermoplastic polyurethane, e.g., ESTANE 5715 to Formulation C is regarded as an optional addition.

However, it has been found that the addition of such a plasticizer causes an increase in flexibility to the dried lacquer coating release layer 20 to make the transferred layer 20 on the article somewhat less subject to cracking if the article is severely bent or distorted. As described in the foregoing, Formulation C is disclosed in patent application Serial No. 181,090 filed April 13, 1988 by the same Assignee of the present application. If Formulation C is used for transfer layer 20, it is prepared by simply mixing the resin oil and plasticizer in a vat at ambient temperatures with the solvent system shown in the Table I for this formulation. The solvents are added typically in a ratio of about 3 to 4 parts solvent to 1 part remaining constituents and the mixing is carried out until a homogeneous mixture is achieved. The mixture then may be coated directly onto thermoset release layer 5 using conventional gravure techniques. After coating, the transfer layer 20 is passed through



convective ovens operating typically between about 175°F to 250°F wherein it is exposed to forced hot air to drive off the solvents and form a tough dry coating layer.

The ink design layer 30 and heat activatable adhesive layer 40 may be composed of conventional formulation known in the art for use in heat transferable laminates of this type. For example, the ink design layer 30 may be composed of any conventional ink of any color. The ink may typically include resinous binder base compatible with the ink pigment employed. The ink binder may be selected from a wide variety of conventional resinous bases such as polyvinylchloride, acrylics, polyamides and nitrocellulose. The ink is applied also by a gravure coating method or the like and then passed through convective ovens for one or two seconds in order to drive off solvents and leave a dried ink design layer 30 over the dried lacquer coating transfer layer 20.

It is advantageous in this technology to overlay ink design layer 30 with a heat activatable adhesive coating 40 which facilitates transfer of the transferable substrate 15 to the article to be decorated. The adhesive layer 40 becomes activatable on exposure to the heat from the hot platen in contact with the support sheet 10 during the transfer process. At the transfer temperature the components in adhesive layer 40 become tacky so that there is sufficient adhesion between the article being decorated and the transferable substrate 15 in contact therewith. Adhesive layer 40 is also applied in solvent base by gravure or other conventional coating methods and the solvent is driven off by exposing the coated layer to convective drying for one or two seconds or sufficient time to evaporate the solvent leaving the dry adhesive coating layer over the ink design layer 30. Adhesive layer 40 may suitably be composed of a thermoplastic polyamide adhesive, preferably a low temperature heat activatable polyamide adhesive.

-24-

A preferred thermoplastic polyamide resin for adhesive layer 40 is the reaction product of a diamine with a dimerized fatty acid such as that available under the tradename VERSAMID 900 Series, or preferably low temperature heat activatable VERSAMID adhesive from Henkel Corp. of Minneapolis, Minnesota. It has been found advantageous to combine this polyamide constituent with a nitrocellulose base in adhesive layer 40. This type of heat activatable adhesive for this particular application is known and documented in the prior art.

In the process of applying heat transfer laminate 7 to an article such as a plastic bottle or container at least 60 such articles per minute may be decorated using the formulations for release layer 5 and lacquer coating transfer layer 20 as shown in Table I. It has been determined that with articles, typically plastic bottles, at least between about [60 to 120] articles per minute may be decorated using the formulations for release layer 5 and lacquer coating transfer layer 20 shown in Table I. In this process, as described in the foregoing, as heat from a hot metal platen or hot rubber platen roller is applied to the exposed side of support sheet 10 while the adhesive layer 40 of laminate 7 comes into contact with the bottle or article to be decorated, transferable substrate 15 separates cleanly from carrier web 2 and separates onto the article. At decoration speeds of between 60 to 120 bottles per minute the carrier web is in direct and intimate contact with the hot platen for at least about 0.25 seconds.

Successful runs using the formulations shown in Table I have also been made at decoration speeds of at least about 60 to 120 bottles per minute with platen average surface temperatures as low as about 275°F and direct contact time between platen and laminate of at least about 0.25 seconds. In this preferred process the laminate 7 is first typically preheated to temperatures of between about 175°F to 225°F before it is contacted with the aforesaid

hot metal platen or hot rubber platen roller. The preheat step is preferably accomplished by passing the laminate 7 over a heated metal surface so that the metal surface contacts the exposed side of support sheet 10 for sufficient time to achieve the desired laminate preheat temperature.

Although the invention has been described within the context of particular embodiments for the transferable laminate, the invention is not intended to be limited to the preferred formulations described herein. Although the lacquer transfer coating layer, for example, has been described with reference to preferred formulations with specific resins together with a small amount of lubricating agent or nondrying oil, the formulation for the lacquer coating layer is not intended to be limited to these particular species of resin and oil respectively. It should also be appreciated that one may add trace or otherwise nonfunctional minor amounts of waxes to layers referenced herein as nonwax layers without being outside the scope of applicant's invention. Thus, the term "nonwax layer" or the equivalent, as used in the foregoing description, is intended to embrace this possibility.

The invention, therefore, is not intended to be limited to the description in the specification but rather is defined by the claims and equivalents thereof.

What is Claimed Is:

-26-

1. A heat transferable laminate comprising a transfer substrate affixed to a carrier sheet for transfer from the carrier sheet to an article upon application of heat to the carrier sheet while said article contacts the transfer substrate, the carrier sheet comprising a support sheet and a nonwax release layer comprising a thermoset alkyd resin coated over said support sheet, the nonwax release layer being in contact with said transfer substrate, said transfer substrate comprising a transfer coating and an ink design layer over the transfer coating, the transfer coating being in contact with said nonwax release layer, said heat transfer laminate having the property that when a heat source is applied to the carrier while said transfer substrate contacts the article said transfer substrate separates cleanly from said nonwax release layer and transfers to said article, the heat transferable laminate having the additional property that no discernible portion of said nonwax release layer is transferred to the article along with said transfer substrate.
2. A heat transferable laminate as in claim 1 wherein the thermoset alkyd resin comprises the crosslinking reaction product of an alkyd polymer with a melamine; wherein said alkyd polymer is formed of the reaction product of a hydroxy-functional ester and an oil, wherein the ester is a noncellulosic ester.
3. A heat transferable laminate as in claim 2 wherein the hydroxy-functional ester comprises the copolymer of monoethylenically unsaturated monomers.
4. A heat transferable laminate as in claim 3 wherein the hydroxy functional ester comprises the copolymer of 2-hydroxyethyl acrylate, lauryl methacrylate and styrene.

5. A heat transferable laminate as in claim 3 wherein the hydroxy functional ester comprises a copolymer of 2-hydroxyethyl acrylate, lauryl methacrylate and methyl methacrylate.

6. A heat transferable laminate as in claim 2 wherein the oil is selected from the group consisting of tung oil, linseed oil, castor oil, safflower oil, cottonseed oil, peanut oil, and coconut oil.

7. A heat transferable laminate as in claim 2 wherein the melamine is hexamethoxymethyl melamine.

8. A heat transferable laminate comprising a transfer substrate affixed to a carrier sheet for transfer from the carrier sheet to an article upon application of heat to the carrier sheet while said article contacts the transfer substrate, the carrier sheet comprising a support sheet and a nonwax release layer comprising a thermoset alkyd resin formed of the crosslinking reaction product of a non-cellulosic alkyd polymer with melamine, the nonwax release layer coated over the support sheet and being in contact with said transfer substrate, said transfer substrate comprising a transfer coating and an ink design over the transfer coating, the transfer coating being in contact with said nonwax release layer, said heat transfer laminate having the property that when a heat source is applied to the carrier while said transfer substrate contacts the article said transfer substrate separates cleanly from said nonwax release layer and transfers to said article, the heat transferable laminate having the additional property that no discernible portion of said nonwax release layer is transferred to the article along with said transfer substrate,

the transfer coating of said transfer substrate comprising a resin selected from the group consisting of vinyl resins, and polyester resins.

-28-

9. A heat transferable laminate as in claim 8 wherein the vinyl resins in said transfer coating comprises polyvinylidene chloride.

10. A heat transferable laminate as in claim 8 wherein the vinyl resin in said transfer coating comprises the copolymer of polyvinylchloride and polyvinylacetate having hydroxyfunctionality permitting crosslinking.

11. A heat transferable laminate as in claim 8 wherein the polyester resin in said transfer coating comprises a polyethylene terephthalate.

12. A heat transferable laminate as in claim 9 wherein the transfer coating further comprises lecithin.

13. A heat transferable laminate as in claim 10 wherein the transfer coating further comprises lecithin.

14. A heat transferable laminate as in claim 8 wherein said alkyd polymer is formed of the reaction product of a hydroxy-functional ester and an oil, wherein the ester is a noncellulosic ester.

15. A heat transferable laminate as in claim 14 wherein the hydroxy functional ester comprises the copolymer of monoethylenically unsaturated monomers.

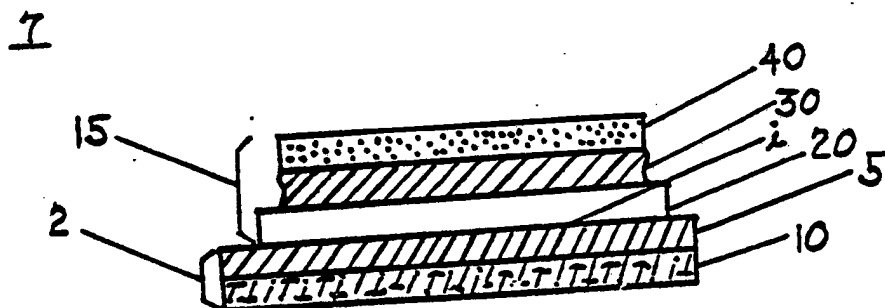
16. A heat transferable laminate as in claim 15 wherein the hydroxy functional ester comprises the copolymer of 2-hydroxyethyl acrylate, lauryl methacrylate and styrene.

17. A heat transferable laminate as in claim 15 wherein the hydroxy functional ester comprises the copolymer of 2-hydroxyethyl acrylate, lauryl methacrylate and methyl methacrylate.

18. A heat transferable laminate as in claim 14 wherein the oil is selected from the group consisting of tung oil, linseed oil, castor oil, safflower oil, tall oil, soya oil, cottonseed oil, peanut oil and coconut oil.

1/1

Fig. 1





# INTERNATIONAL SEARCH REPORT

International Application No. **PCT/US89/01731**

## I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) <sup>6</sup>

According to International Patent Classification (IPC) or to both National Classification and IPC

**IPC(4) B05D 3/04**

**U.S. CL. 428/195**

## II. FIELDS SEARCHED

Minimum Documentation Searched <sup>7</sup>

Classification System	Classification Symbols
<b>U.S.</b>	<b>428/195, 200, 201, 204, 423.1, 524, 913, 914</b>

Documentation Searched other than Minimum Documentation  
to the Extent that such Documents are Included in the Fields Searched <sup>8</sup>

## III. DOCUMENTS CONSIDERED TO BE RELEVANT <sup>9</sup>

Category <sup>10</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
Y	US, A, 4,118,541 (POWER ET AL) 3 OCTOBER 1978 SEE THE ENTIRE DOCUMENT	1-18
Y	US, A, 4,117,198 (POWER ET AL) 26 SEPTEMBER 1978 SEE THE ENTIRE DOCUMENT	1-18

### \* Special categories of cited documents: <sup>10</sup>

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"Δ" document member of the same patent family

## IV. CERTIFICATION

Date of the Actual Completion of the International Search

**11 SEPTEMBER 1989**

International Searching Authority

**ISA/US**

Date of Mailing of this International Search Report

**28 SEP 1989**

Signature of Authorized Officer

**P.J. RYAN**